

AH Chemistry – Unit 1

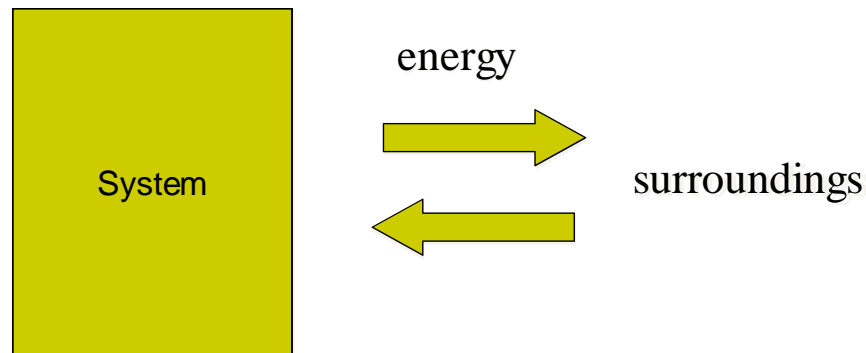
Reaction Feasibility

THERMOCHEMISTRY

The study of changes in ENERGY which occur during chemical reactions

First Law Of Thermodynamics

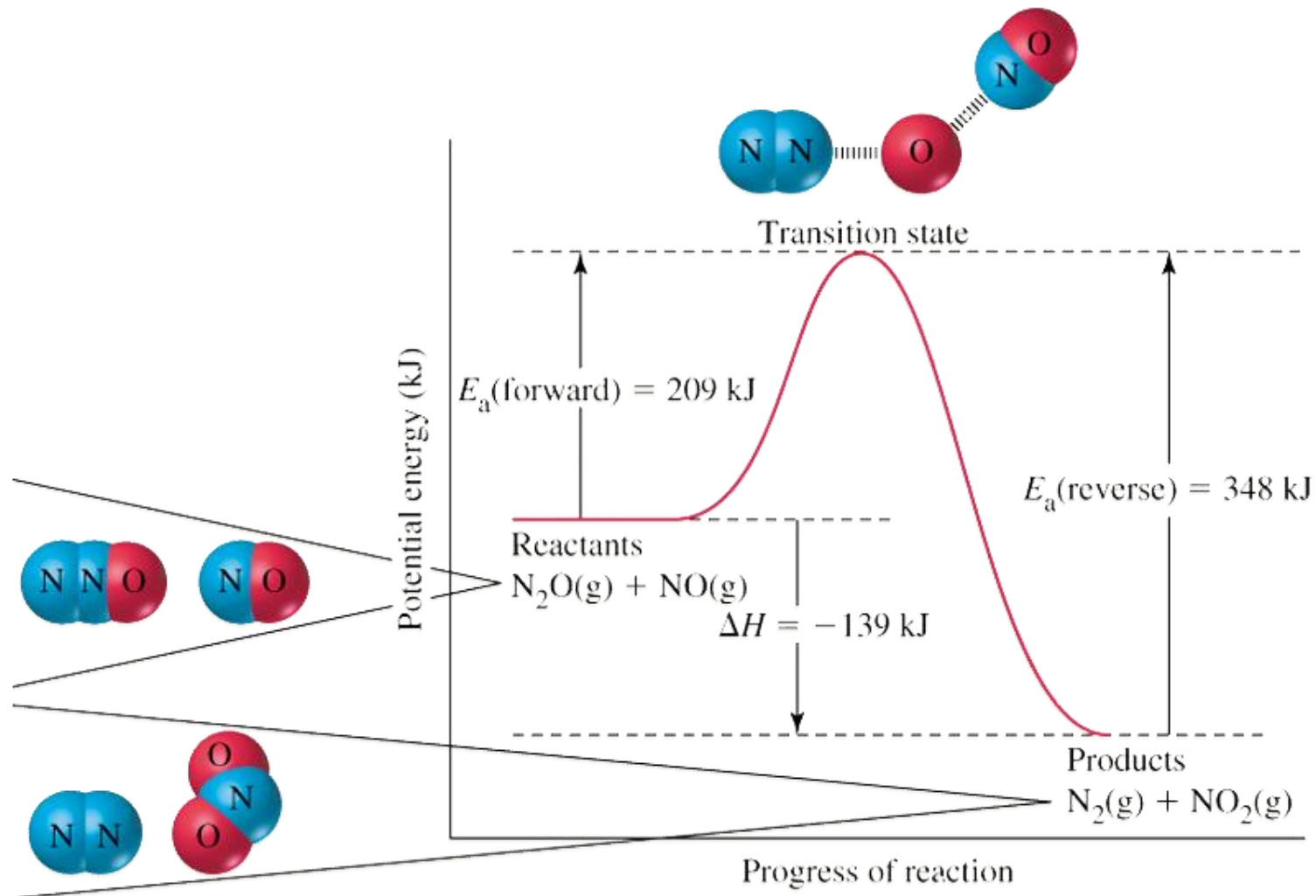
The *Total Energy* of the Universe (System and Surroundings) *is constant*



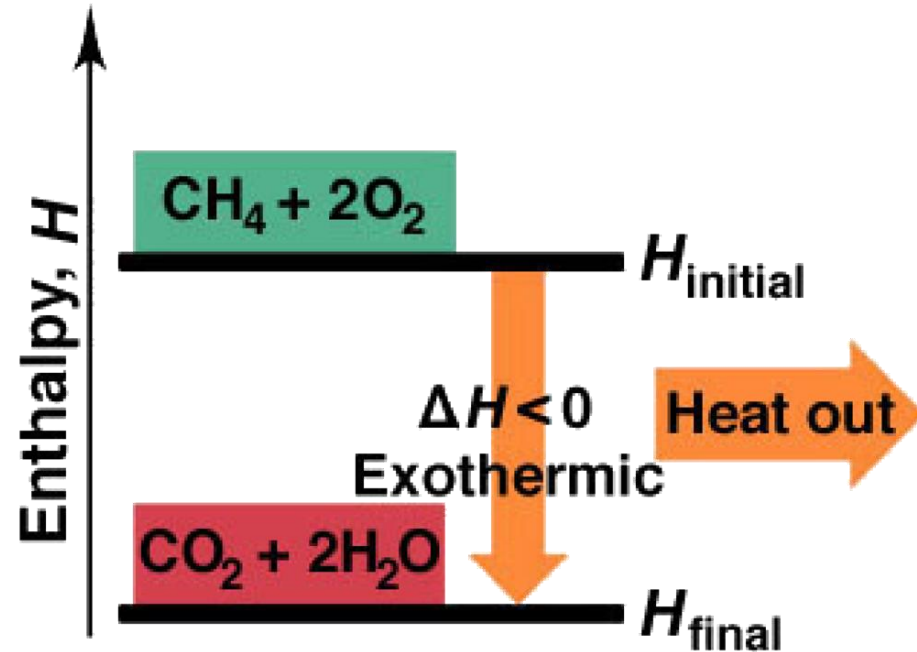
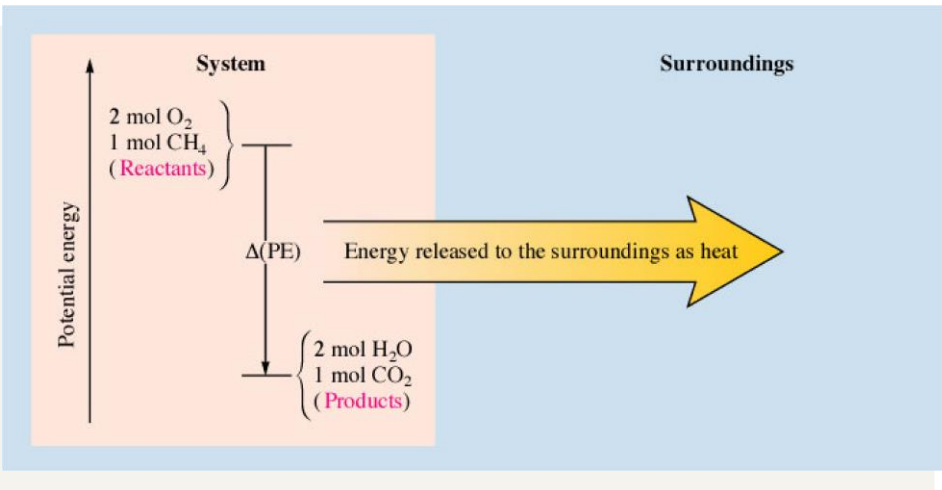
Energy can *neither be created nor destroyed*

Energy *can be converted* from one Form to another while the Total Energy remains the same

Energy Pathway Diagrams

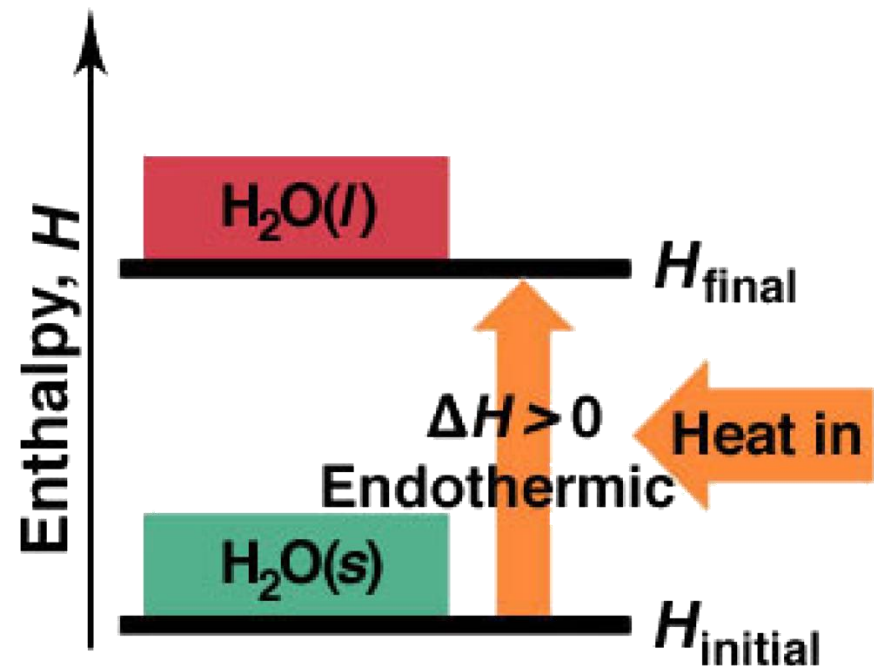


Enthalpy ~ Exothermic

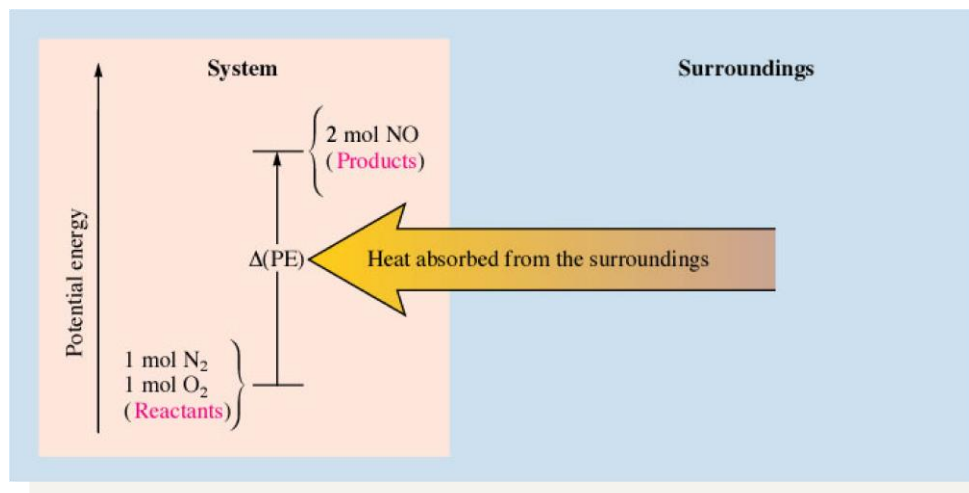


$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

Enthalpy ~ Endothermic



$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$



Actual Enthalpy values, H ,
cannot be measured.

Changes in Enthalpy, ΔH ,
can be measured.

Standard Enthalpies

reactants and products are in their *standard states*

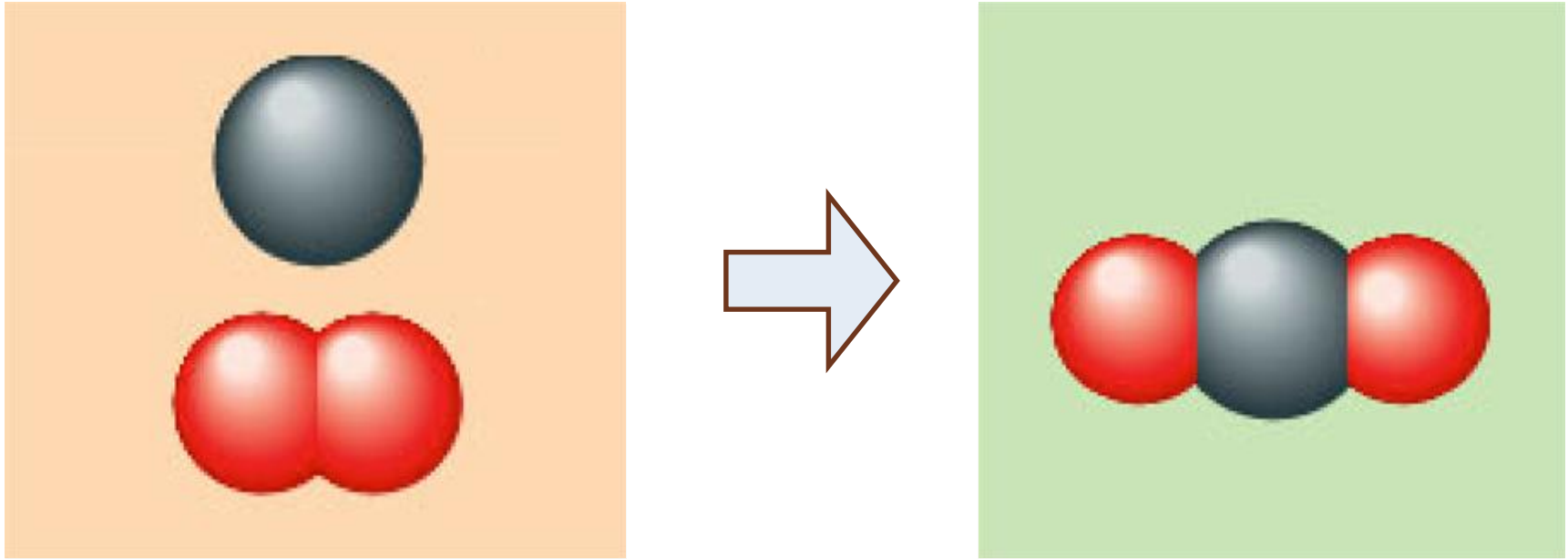
measured at a *specific temperature*, usually 298K

measured at a pressure of *one atmosphere*, 10^5 Nm^{-2}

concentrations of solutions are *one mol l⁻¹*

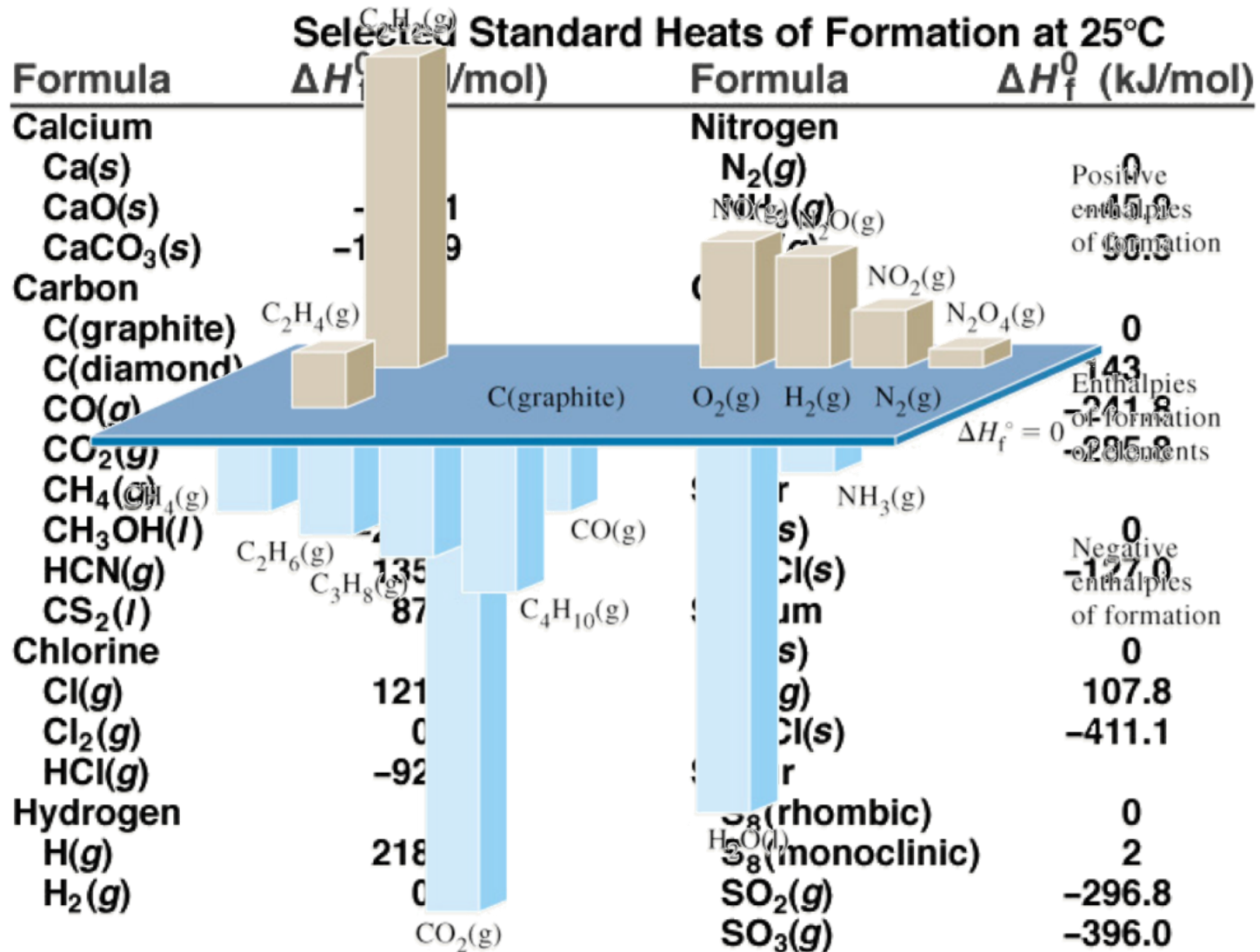
designated using superscript [°], ΔH°

Enthalpy of Formation



is the *heat change* when *1 mole* of a *compound* is *formed from its elements* under *standard conditions*

Standard Enthalpies of Formation



Named Enthalpies

Combustion

Atomisation

Lattice Forming

Ionisation

Solution

Solvation

Neutralisation

Hydration

Formation

Bond Breaking

Lattice Breaking

Bond Forming

Fusion

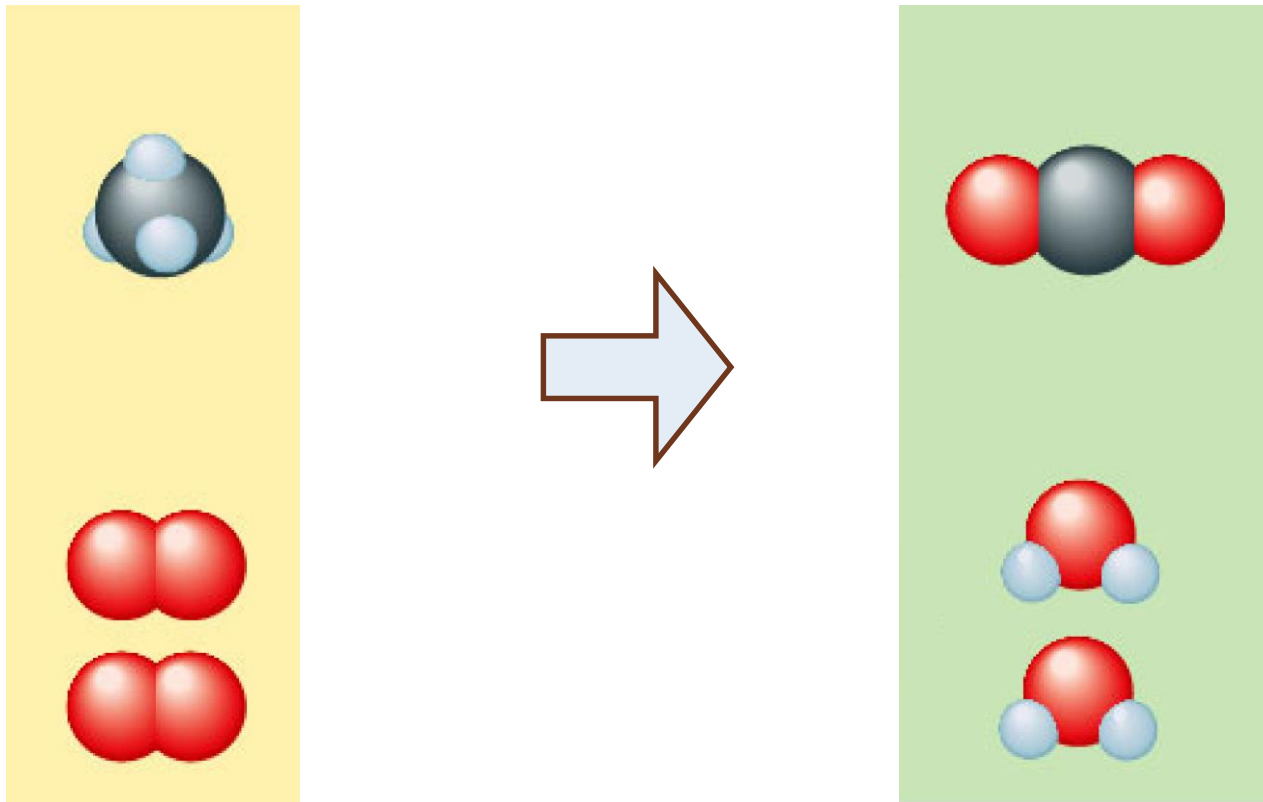
Sublimation

Vaporisation

Named Enthalpies

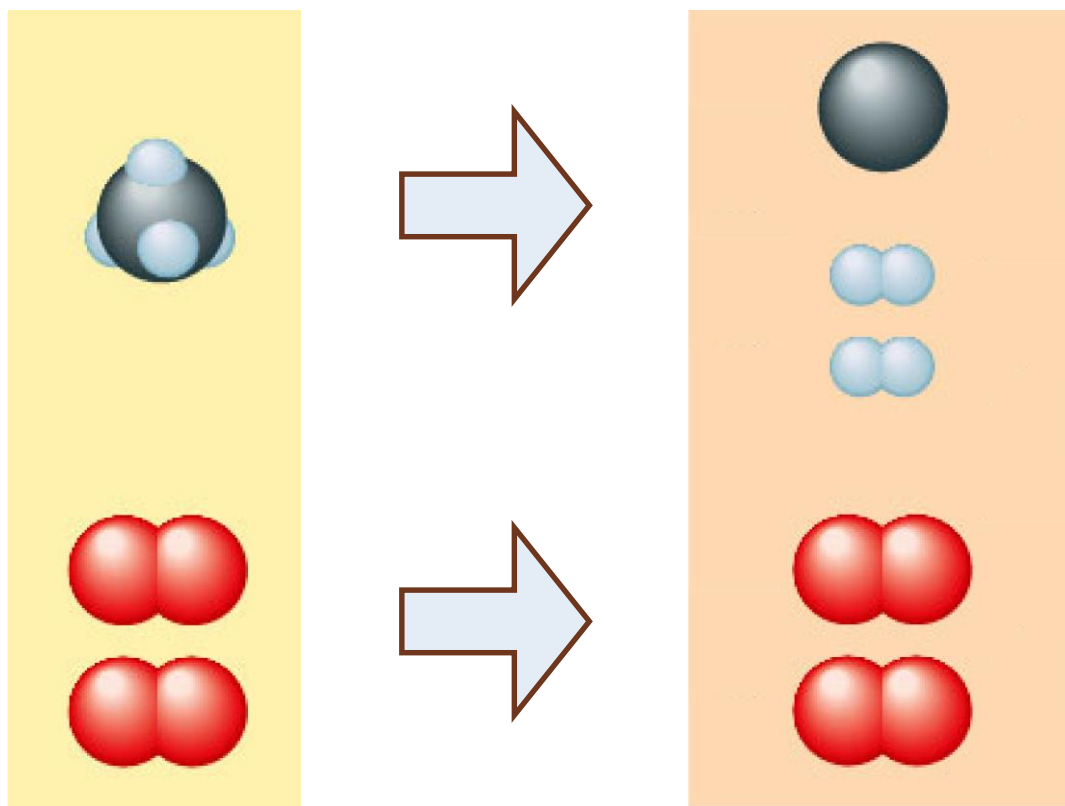
Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{\text{trs}}H$
Fusion	$s \rightarrow l$	$\Delta_{\text{fus}}H$
Vaporization	$l \rightarrow g$	$\Delta_{\text{vap}}H$
Sublimation	$s \rightarrow g$	$\Delta_{\text{sub}}H$
Mixing	Pure \rightarrow mixture	$\Delta_{\text{mix}}H$
Solution	Solute \rightarrow solution	$\Delta_{\text{sol}}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{\text{hyd}}H$
Atomization	Species(s, l, g) \rightarrow atoms(g)	$\Delta_{\text{at}}H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{\text{ion}}H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{\text{eg}}H$
Reaction	Reactants \rightarrow products	$\Delta_{\text{r}}H$
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_{\text{c}}H$
Formation	Elements \rightarrow compound	$\Delta_{\text{f}}H$
Activation	Reactants \rightarrow activated complex	$\Delta^{\ddagger}H$

Using Enthalpies of Formation



The *Enthalpy of Combustion* of methane can be *calculated* using *Enthalpies of Formation*

Step1 : Reactants to Elements

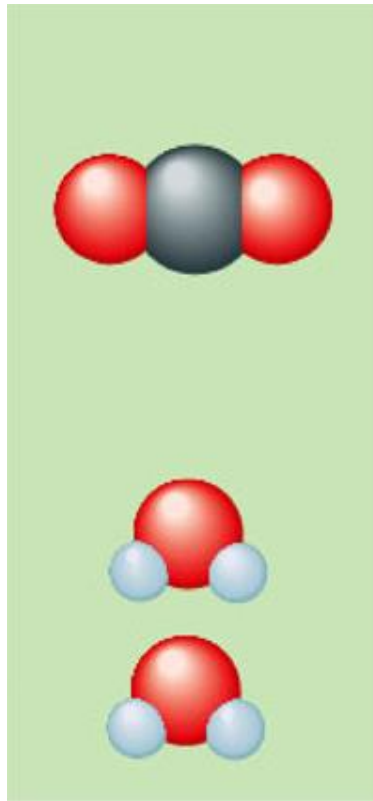
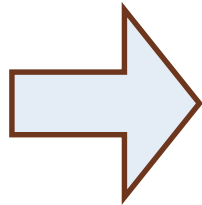
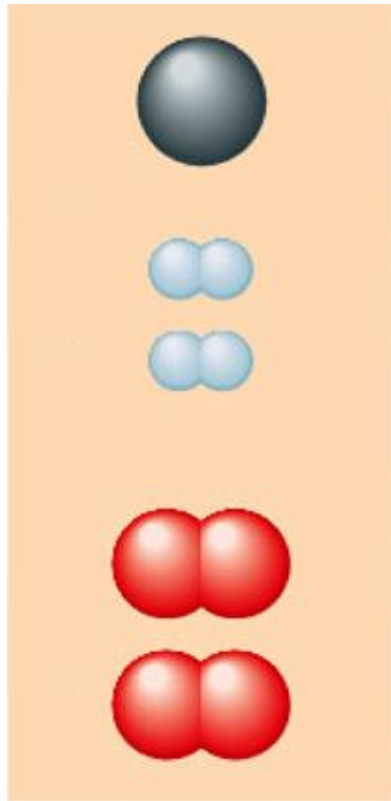


This is the ΔH° of methane *reversed*.

By definition, the ΔH° of an element = zero *f*

$$\Delta H_{\text{step 1}} = - (\Delta H^\circ_{f \text{ methane}} + \Delta H^\circ_{f \text{ oxygen}}) = - \sum \Delta H^\circ_{f \text{ reactants}}$$

Step2 : Elements to Products

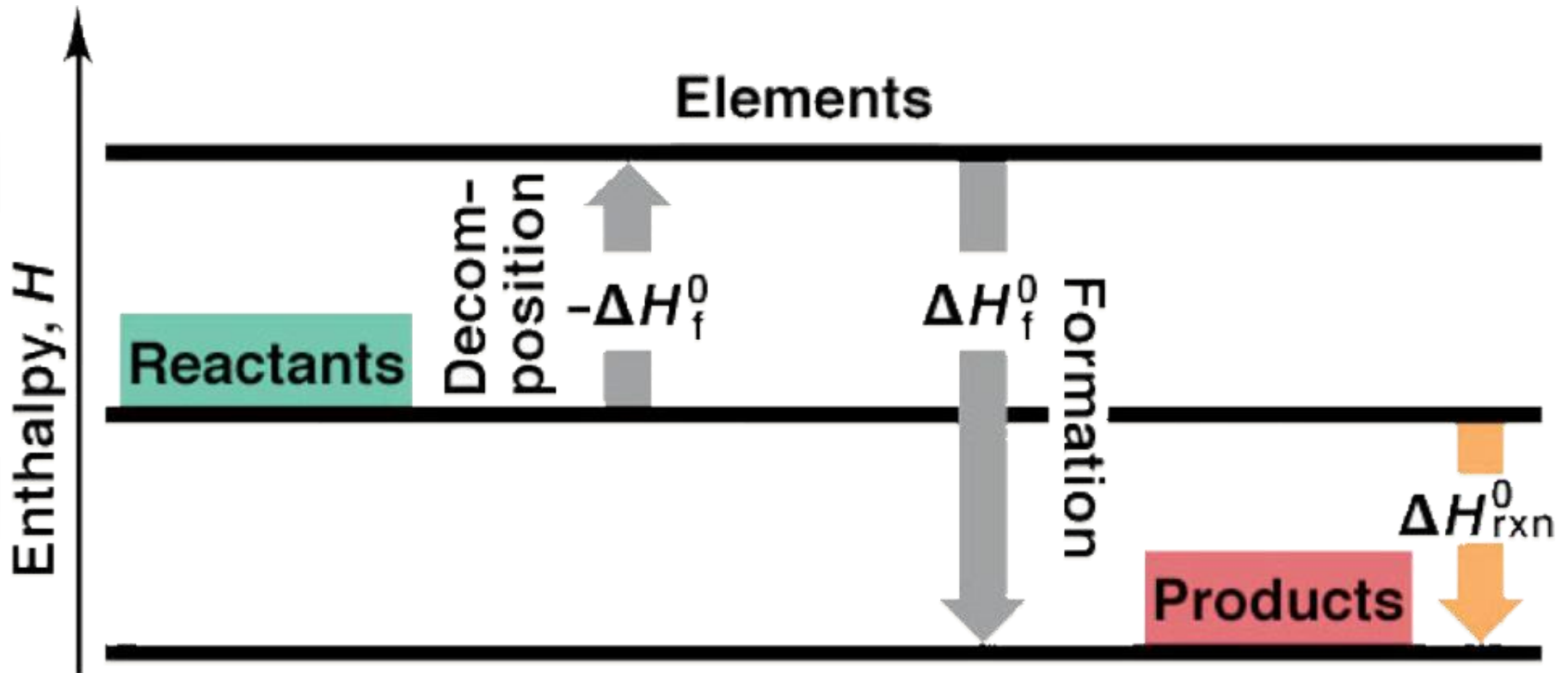


This is the ΔH°_f of carbon dioxide.

This is the $2 \times \Delta H^\circ_f$ of water.

$$\Delta H_{\text{step 2}} = (\Delta H^\circ_f \text{ CO}_2 + 2 \times \Delta H^\circ_f \text{ water}) = \sum \Delta H^\circ_f \text{ products}$$

General Expression

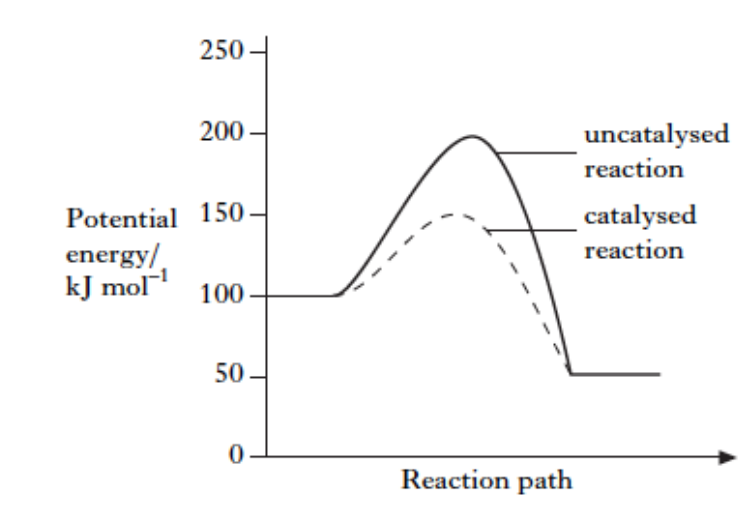


$$\Delta H_{reaction} = \Delta H_{step 1} + \Delta H_{step 2}$$

$$\Delta H_{reaction} = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

Formulae

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

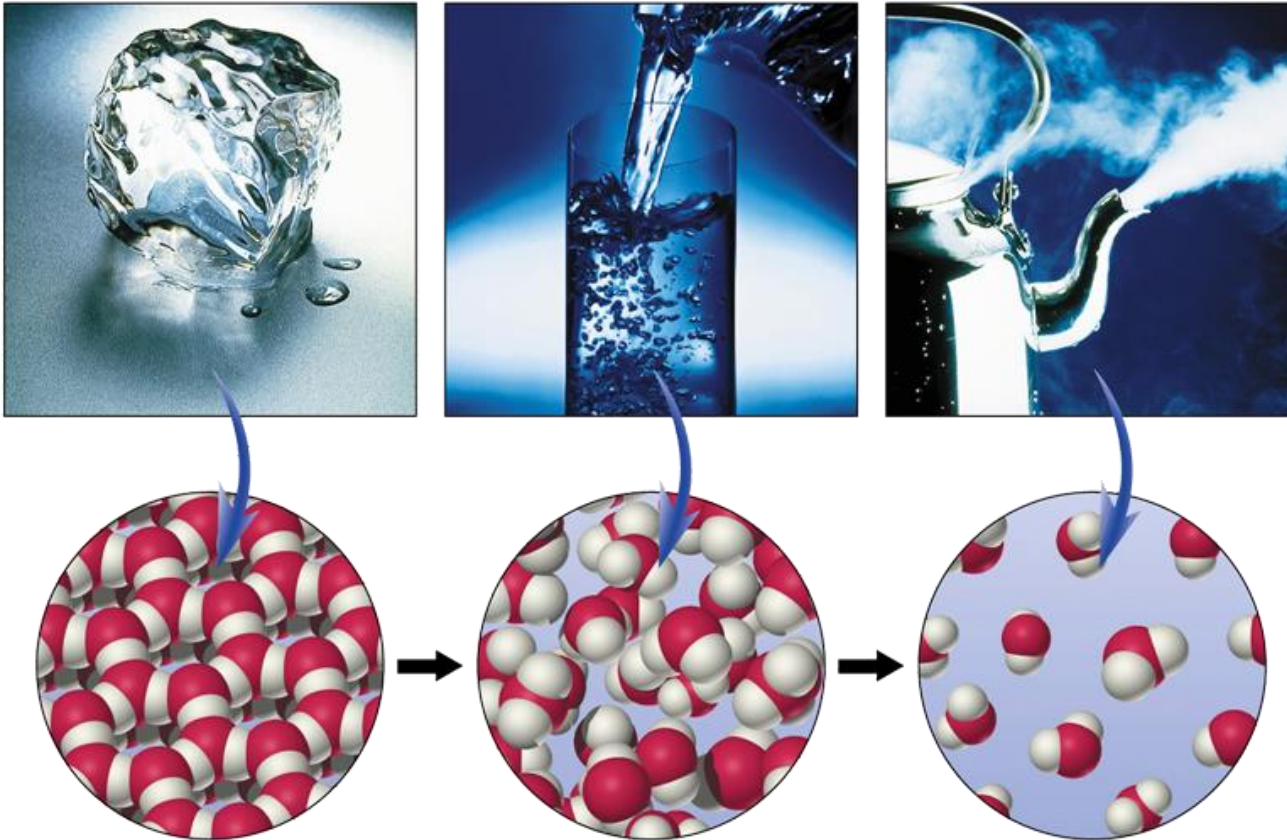


$$\Delta H_{\text{reaction}} = \sum \Delta H^{\circ} f_{\text{products}} - \sum \Delta H^{\circ} f_{\text{reactants}}$$

$$\Delta H_{\text{reaction}} = \sum \text{Bond Breaking (reactants)} + \sum \text{Bond Forming (products)}$$

Energy Rules!

Some Processes involve **no change in temperature** but a major change in the energy of particles is still occurring.

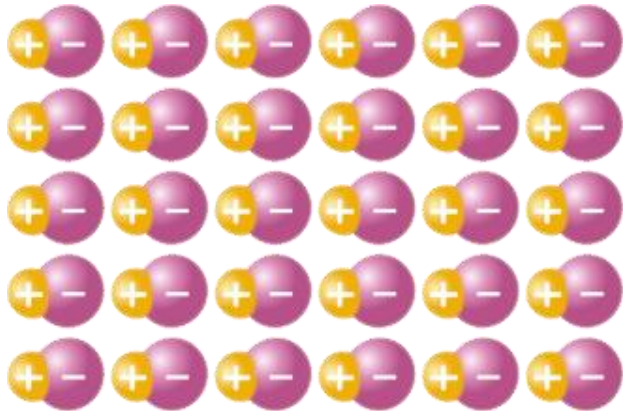


Entropy

These changes in the energy of particles have an overall affect on the **level of disorder** shown by a substance.

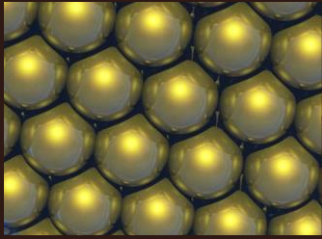
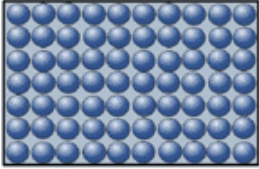
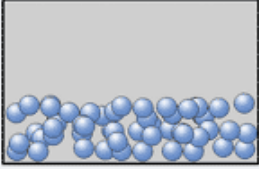
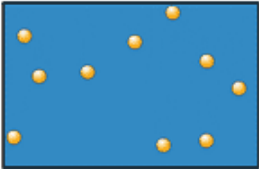
The disorder in a substance is known as its **ENTROPY, S**.

The **Third Law of Thermodynamics** provides a reference against which **Entropies** can be measured.

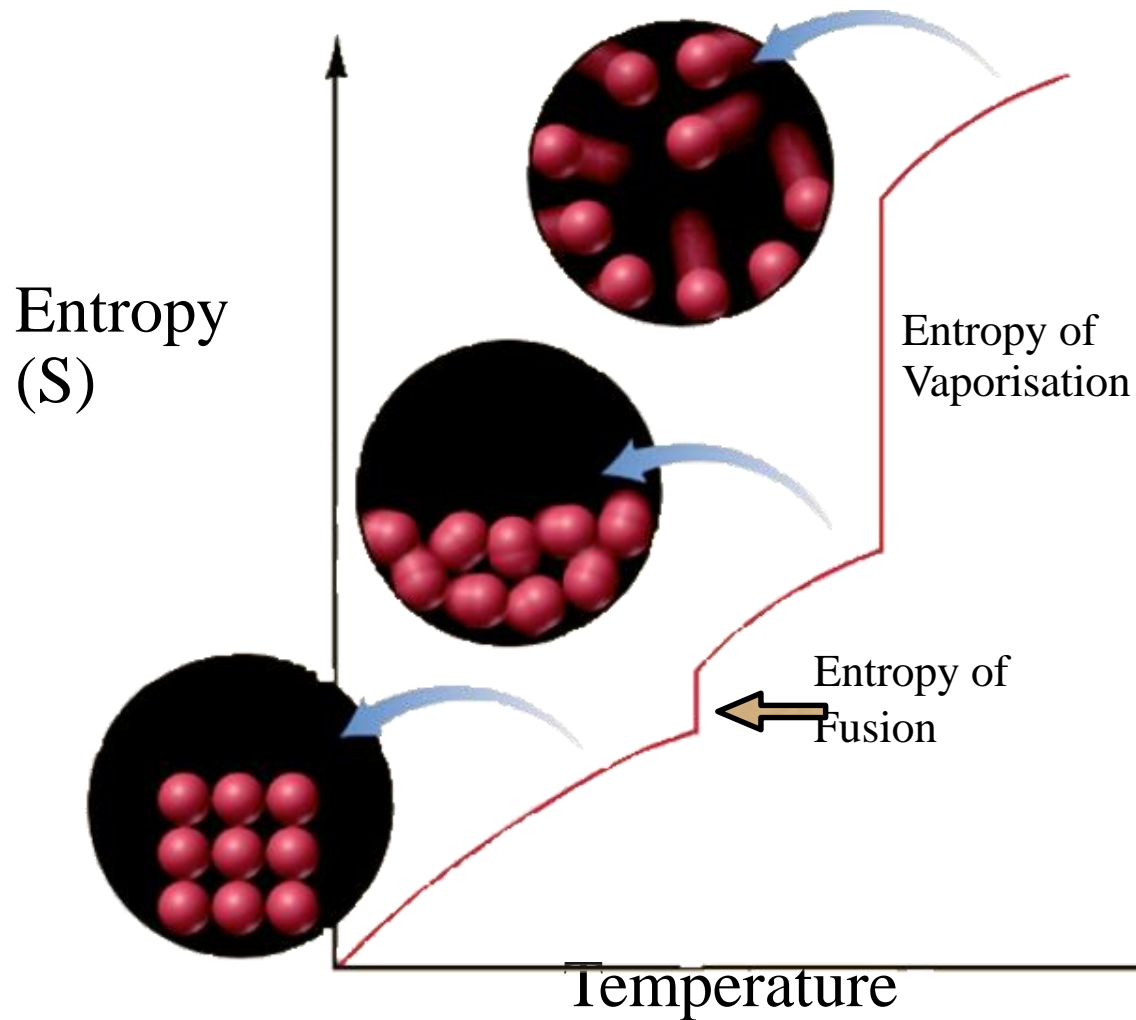


“the **Entropy** of a perfect crystal at 0 K is **zero**”

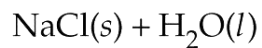
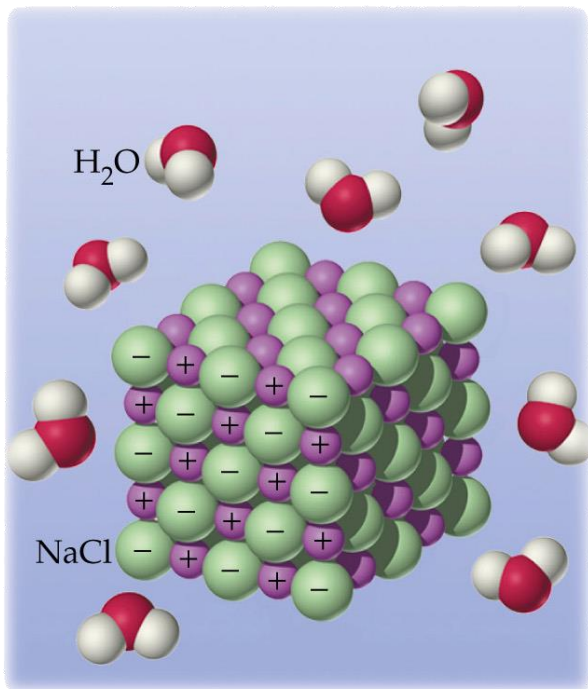
Entropy - State

	Molecular Motion		
	Translation	Rotation	Vibration
<p>Kinetic Energy - Solid</p> 	no freedom to move	no freedom to rotate	free to vibrate
<p>Kinetic Energy - Liquid</p> 	restricted freedom to move	some freedom to rotate	free to vibrate
<p>Kinetic Energy - Gas</p>  <p>HEAT</p>	total freedom to move	total freedom to rotate	free to vibrate

Entropy - Temperature

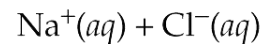
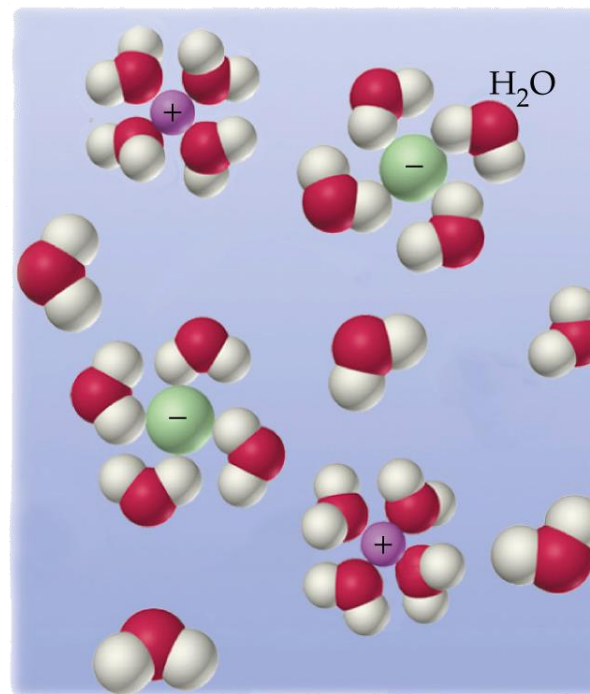


Entropy - Dissolving



Less Randomness

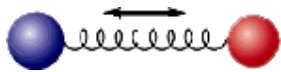
Less Entropy



More Randomness

More Entropy

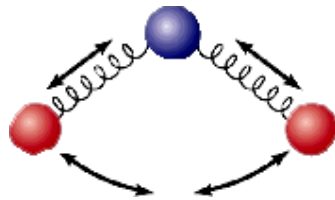
Entropy - Molecules



NO

Fewer
Vibrations

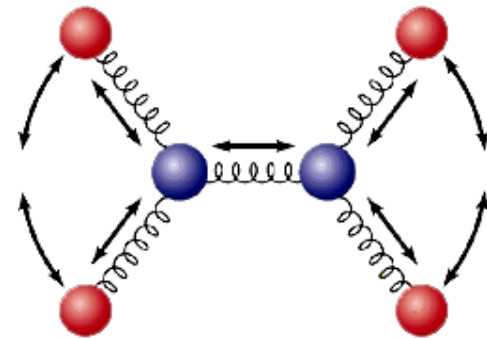
Less Entropy



NO₂

More Vibrations

More Entropy

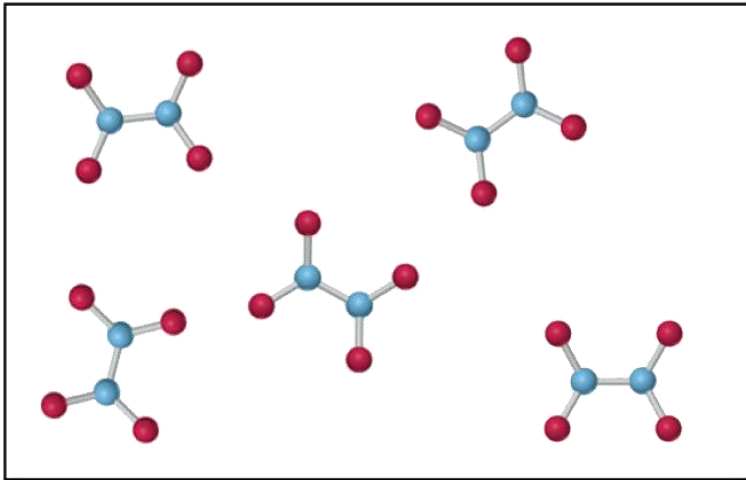


N₂O₄

More Vibrations

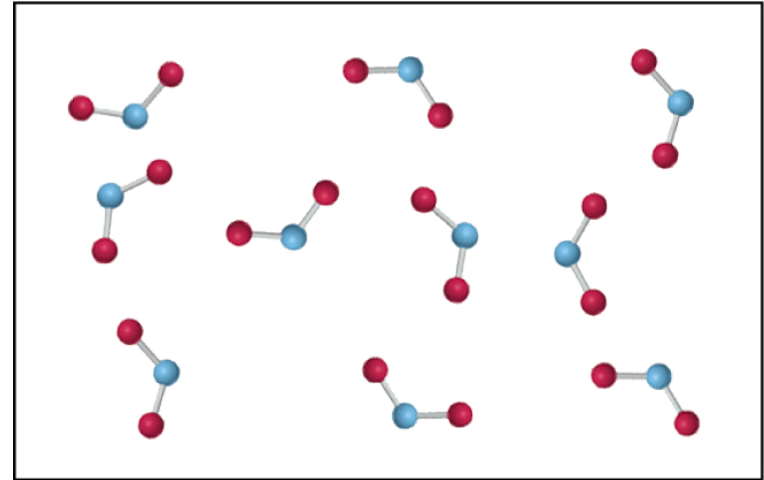
More Entropy

Entropy - Numbers



Less Randomness

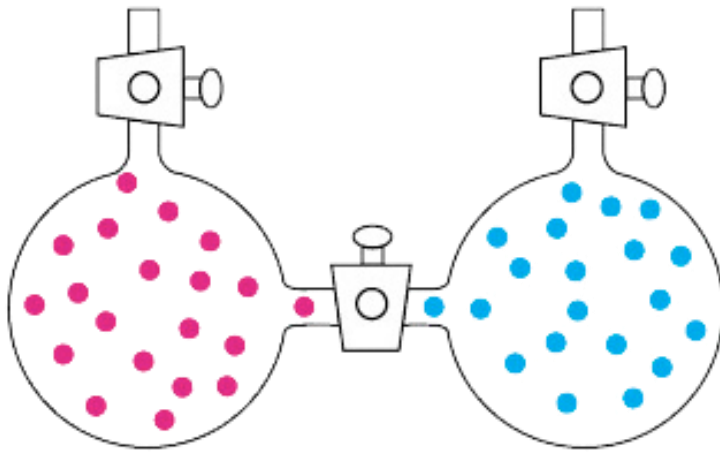
Less Entropy



More Randomness

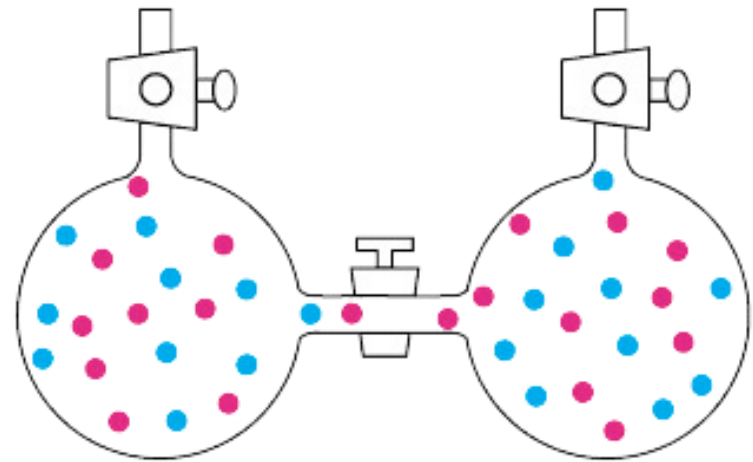
More Entropy

Entropy - Mixtures



Less Randomness

Less Entropy



More Randomness

More Entropy

Entropy Values

Standard Molar Entropies for Some Common Substances at 25°C

Substance	Formula	S° [J/(K · mol)]	Substance	Formula	S° [J/(K · mol)]
Gases			Liquids		
Acetylene	C ₂ H ₂	200.8	Acetic acid	CH ₃ CO ₂ H	160
Ammonia	NH ₃	192.3	Ethanol	CH ₃ CH ₂ OH	161
Carbon dioxide	CO ₂	213.6	Methanol	CH ₃ OH	127
Carbon monoxide	CO	197.6	Water	H ₂ O	69.9
Ethylene	C ₂ H ₄	219.5	Solids		
Hydrogen	H ₂	130.6	Calcium carbonate	CaCO ₃	92.9
Methane	CH ₄	186.2	Calcium oxide	CaO	39.7
Nitrogen	N ₂	191.5	Diamond	C	2.4
Nitrogen dioxide	NO ₂	240.0	Graphite	C	5.7
Dinitrogen tetroxide	N ₂ O ₄	304.2	Iron	Fe	27.3
Oxygen	O ₂	205.0	Iron(III) oxide	Fe ₂ O ₃	87.4

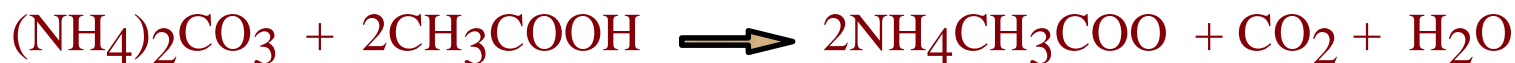
Entropy Calculations

Similar to a previous formula:

$$\Delta S^{\circ} = \sum S^{\circ}_{\text{products}} - \sum S^{\circ}_{\text{reactants}}$$

Entropy Changes, ΔS

- spontaneous endothermic reactions tend to have certain characteristics in common



- the number of moles of product are **greater than** the number of moles of reactant
- a large proportion of the products are either **liquids** or **gases**
- reactants are often **solids** or **liquids**

The trend **solids** \longrightarrow **liquids** \longrightarrow **gases** is associated with an **increase in disorder** .

Entropy - The Answer?

Is an **Increase In Entropy** the driving force behind a spontaneous chemical reaction ?



Solid water

$$\begin{array}{ll} \Delta S^\circ = +22.0 \text{ J}/(\text{K} \cdot \text{mol}) & \text{(Entropy increases)} \\ \Delta H^\circ = +6.01 \text{ kJ/mol} & \text{(Endothermic)} \end{array}$$

Spontaneous above 0°C

$$\begin{array}{ll} \Delta S^\circ = -22.0 \text{ J}/(\text{K} \cdot \text{mol}) & \text{(Entropy decreases)} \\ \Delta H^\circ = -6.01 \text{ kJ/mol} & \text{(Exothermic)} \end{array}$$

Spontaneous below 0°C

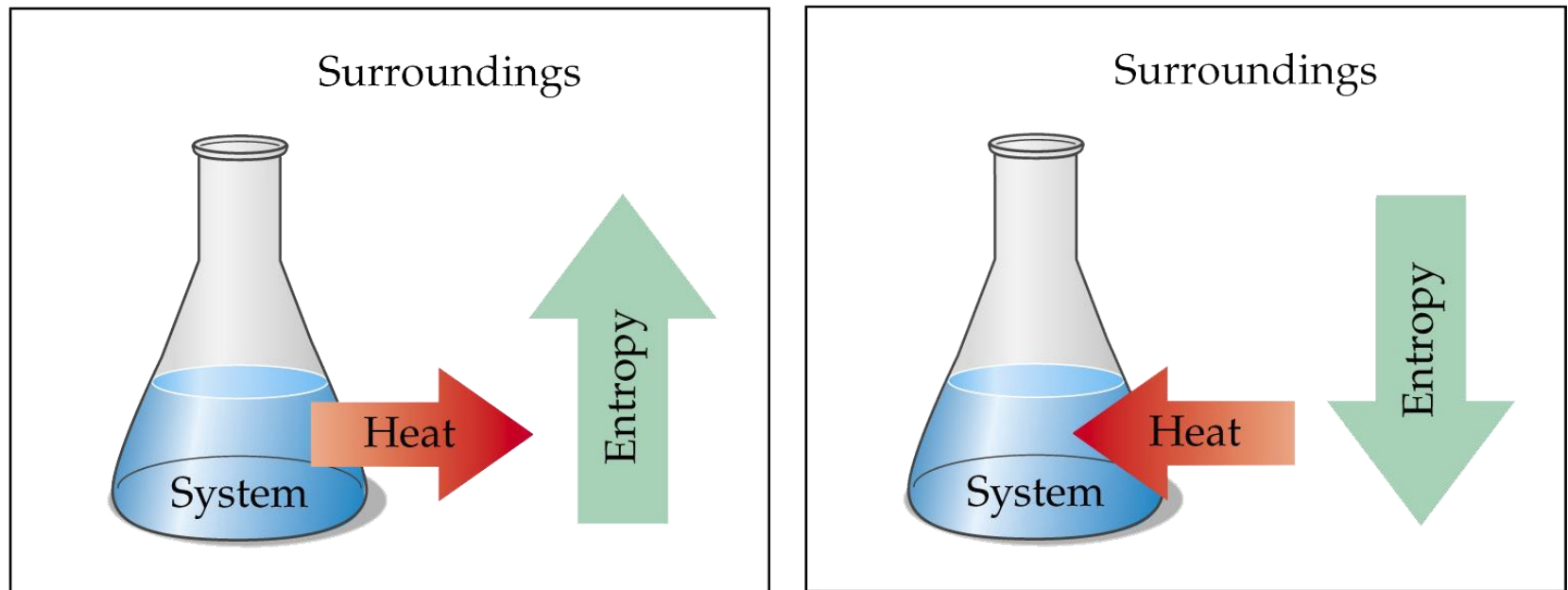


Liquid water

Both $\Delta S = +ve$ & $\Delta S = -ve$ processes can be **spontaneous**
The direction of a **spontaneous** process will **depend on temperature**
A **spontaneous** process will **depend on both ΔS and ΔH**

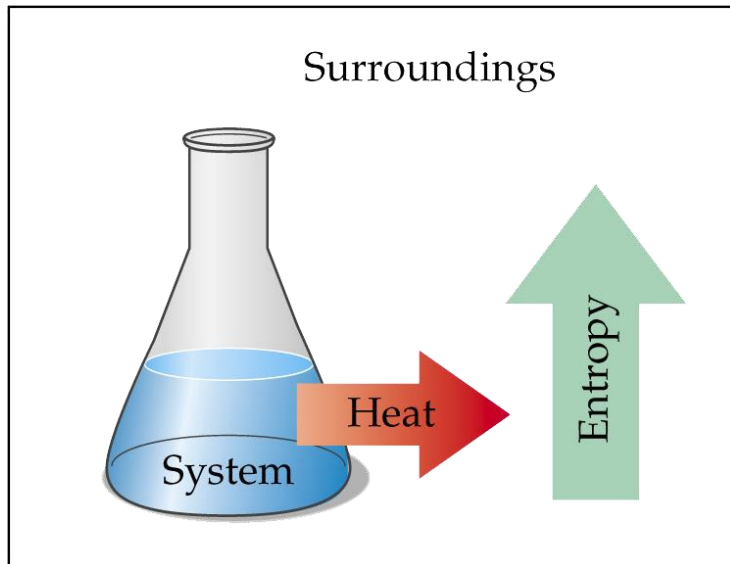
Entropy - The Answer?

The 'problem' can be resolved if we take into account changes taking place in the **Surroundings**.



The driving force behind a spontaneous process turns out to be an **Overall Increase In Entropy**

Entropy - The Answer?

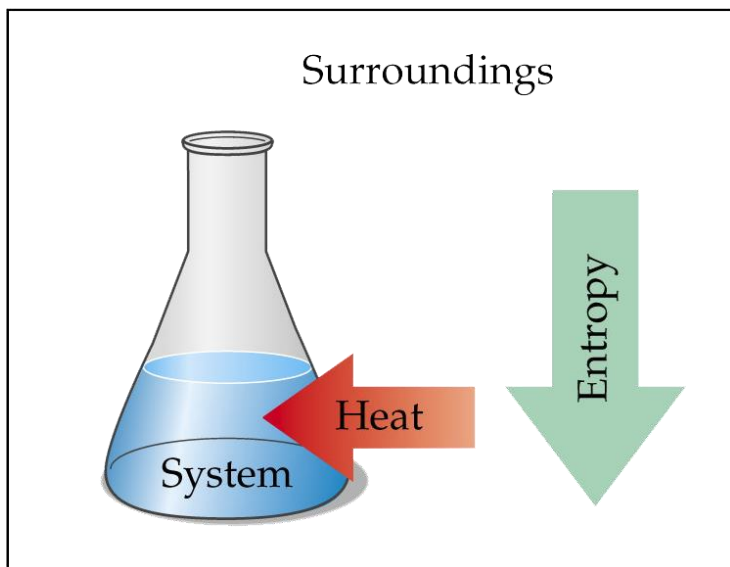


Water freezing leads to a **decrease in entropy** within the **system**.

Being Exothermic, however, leads to an **increase in entropy** in the **surroundings**

Water freezing is a spontaneous process whenever there is an **Overall Increase In Entropy**

Entropy - The Answer?



Being Endothermic leads to a decrease in entropy in the surroundings

There will have to be an increase in entropy within the system.

Water melting is a spontaneous process whenever there is an **Overall Increase In Entropy**

Measuring $\Delta S^\circ_{\text{surr}}$

Trying to Calculate the effect on the surroundings would appear, at first, an impossible task.

Where do the surroundings start & finish?

What is the entropy of air? Glass? etc.

How many moles of ‘surroundings’ are there?

Fortunately it is much, much simpler than that.

Measuring $\Delta S^\circ_{\text{surr}}$

Firstly the change in Entropy of the Surroundings is caused by the Enthalpy change of the Surroundings, and.....

$$\Delta H^\circ_{\text{surr}} \equiv -\Delta H^\circ_{\text{syst}}$$

$$\text{so } \Delta S^\circ_{\text{surr}} \propto -\Delta H^\circ_{\text{syst}}$$

Temperature has an inverse effect. For example, energy released into the surroundings has less effect on the entropy of the surroundings, the hotter the surroundings are.

Measuring $\Delta S^\circ_{\text{surr}}$

In fact, it turns out that ..

$$\Delta S^\circ_{\text{surr}} = -\frac{\Delta H^\circ_{\text{syst}}}{T}$$

It is the **Overall Entropy Change** that must be considered.

$$\Delta S^\circ_{\text{total}} = \Delta S^\circ_{\text{syst}} + \Delta S^\circ_{\text{surr}}$$

$$\Delta S^\circ_{\text{total}} = \Delta S^\circ_{\text{surr}} - \frac{\Delta H^\circ_{\text{syst}}}{T}$$

Measuring $\Delta S^{\circ}_{\text{total}}$

We are interested in the point at which the **Total Entropy** becomes a positive value (ceases being a negative value). We can 'solve' for

$$\Delta S_{\text{total}} = 0$$

$$0 = \Delta S^{\circ}_{\text{surr}} - \frac{\Delta H^{\circ}_{\text{syst}}}{T}$$

Multiplying throughout by **T** gives us

$$0 = T\Delta S^{\circ}_{\text{syst}} - \Delta H^{\circ}_{\text{syst}}$$

Measuring $\Delta S^\circ_{\text{total}}$

Remember that this is really the formula for ΔS_{total}

$$\Delta S^\circ_{\text{total}} = T\Delta S^\circ_{\text{syst}} - \Delta H^\circ_{\text{syst}}$$

Armed with ΔS , ΔH and values for T we can calculate the overall change in Entropy and a positive value would be necessary for a spontaneous reaction.

However, for reasons that are beyond this Topic, a term called the **Gibbs Free Energy, G**, is preferred. A **negative value** for ΔG is equivalent to a **positive value** for ΔS . This requires a slight adjustment in our final formula.

Gibbs Free Energy ΔG°

$$\Delta G^\circ = \Delta H^\circ_{\text{syst}} - T\Delta S^\circ_{\text{syst}}$$

The convenient thing about this expression is that it allows us to do calculations using only values that can be directly measured or easily calculated.

Strictly speaking, the **Second Law of Thermodynamics** states that **Entropy must increase** for a Spontaneous Process.

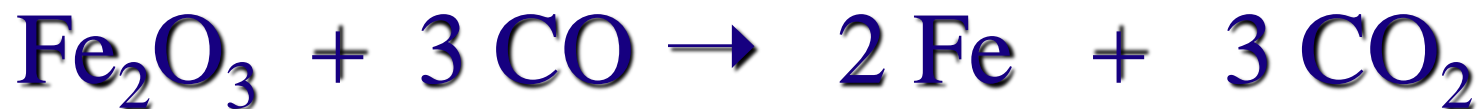
In practice, the **Second Law of Thermodynamics** means that **Gibbs Free Energy must decrease** for a Spontaneous Process.

Gibbs Free Energy ΔG°

Signs of Enthalpy, Entropy, and Free-Energy Changes and Reaction Spontaneity at Constant Temperature and Pressure

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Reaction Spontaneity
-	+	-	Spontaneous at all temperatures
-	-	- or +	Spontaneous at low temperatures where ΔH outweighs $T\Delta S$ Nonspontaneous at high temperatures where $T\Delta S$ outweighs ΔH
+	-	+	Nonspontaneous at all temperatures
+	+	- or +	Spontaneous at high temperatures where $T\Delta S$ outweighs ΔH Nonspontaneous at low temperatures where ΔH outweighs $T\Delta S$

Calculating ΔG°



	Fe₂O₃(s)	CO(g)	Fe(s)	CO₂(g)
ΔH°_f (kJ/mol)	-824.2	-110.5	0	-393.5
S° [J/(K·mol)]	87.4	197.6	27.3	213.6

$$\Delta H^\circ = \sum \Delta H^\circ_{f, \text{products}} - \sum \Delta H^\circ_{f, \text{reactants}}$$

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

T in Kelvin $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

ΔG° of Formation

$$\Delta G^\circ = \sum \Delta G_{f}^\circ \text{ products} - \sum \Delta G_{f}^\circ \text{ reactants}$$

Standard Free Energies of Formation for Some Common Substances at 25°C

Substance	Formula	ΔG_f° (kJ/mol)	Substance	Formula	ΔG_f° (kJ/mol)
Gases			Liquids		
Acetylene	C ₂ H ₂	209.2	Acetic acid	CH ₃ CO ₂ H	-390
Ammonia	NH ₃	-16.5	Ethanol	C ₂ H ₅ OH	-174.9
Carbon dioxide	CO ₂	-394.4	Methanol	CH ₃ OH	-166.4
Carbon monoxide	CO	-137.2	Water	H ₂ O	-237.2
Ethylene	C ₂ H ₄	68.1	Solids		
Hydrogen	H ₂	0	Calcium carbonate	CaCO ₃	-1128.8
Methane	CH ₄	-50.8	Calcium oxide	CaO	-604.0
Nitrogen	N ₂	0	Diamond	C	2.9
Nitrogen dioxide	NO ₂	51.3	Graphite	C	0
Dinitrogen tetroxide	N ₂ O ₄	97.8	Iron(III) oxide	Fe ₂ O ₃	-742.2

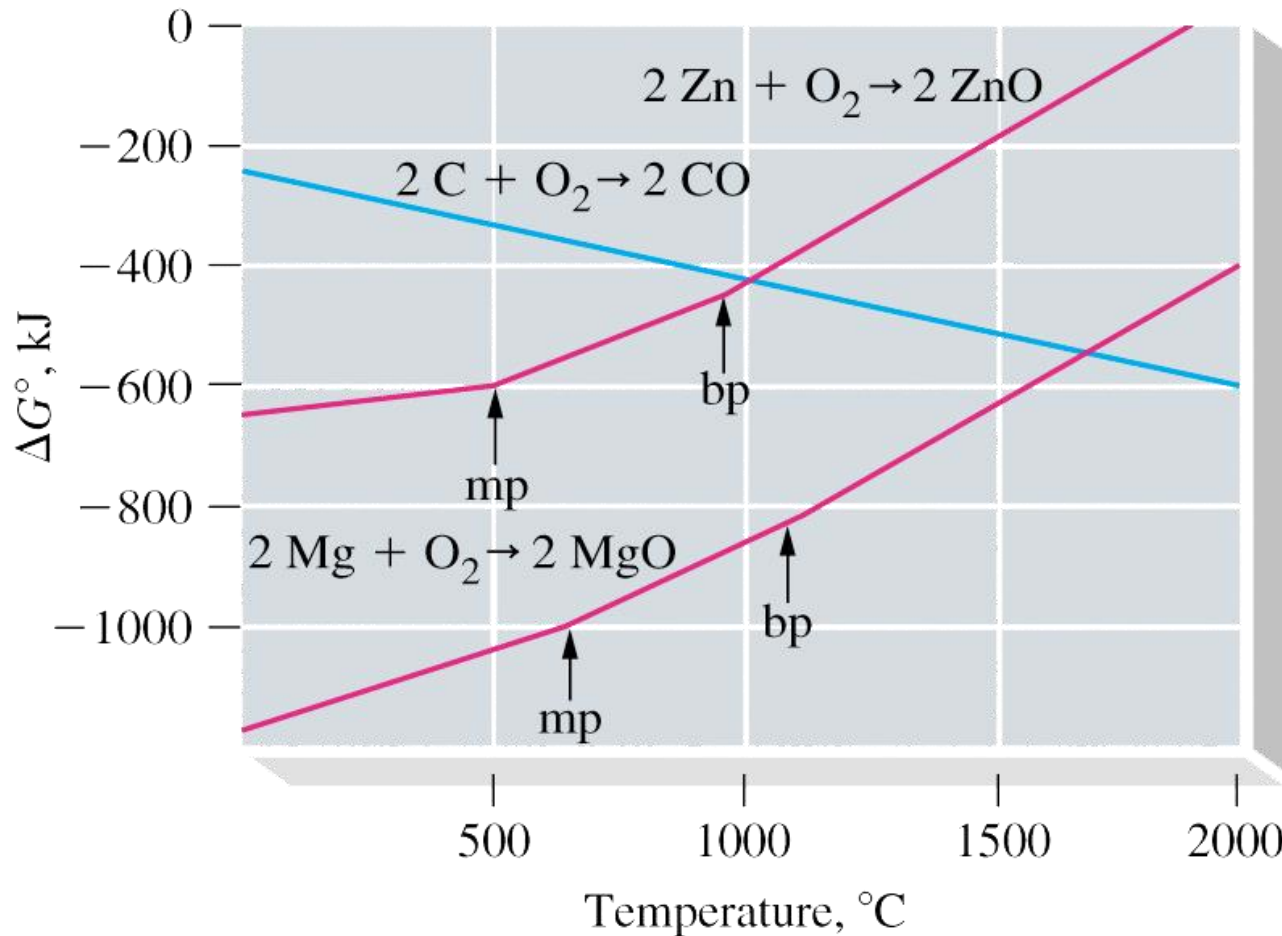
The ΔG of a reaction can be calculated from ΔG_f values.

By themselves, they give useful information about **relative stabilities**.

Ellingham Diagrams

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$y = c + mx$$



Reversible Reactions

For a Chemical Reaction

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

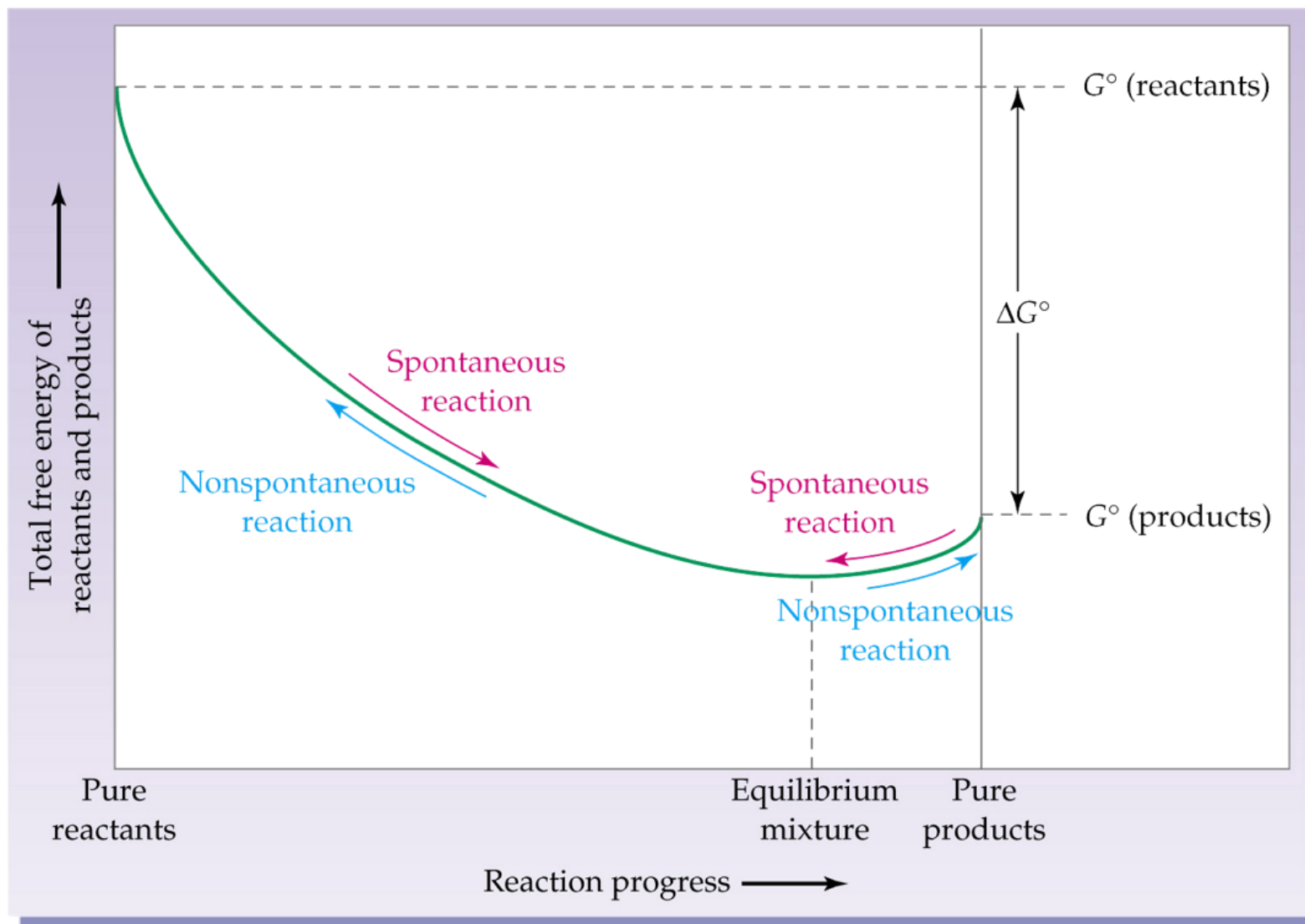
If ΔG is **negative** for one direction, it must be **positive** for the reverse.

This implies that only one reaction can proceed (spontaneously) under a given set of conditions.

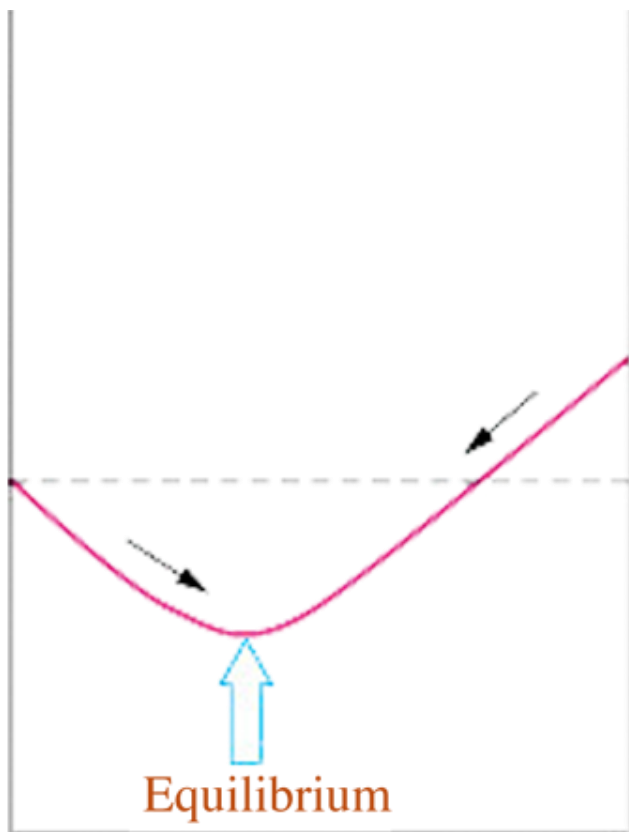
However, ΔS calculations are based on 100% Reactant & 100% Product.

In reality, mixtures exist, so larger ΔS values will be obtained than those calculated.

Reversible Reactions



Equilibrium position

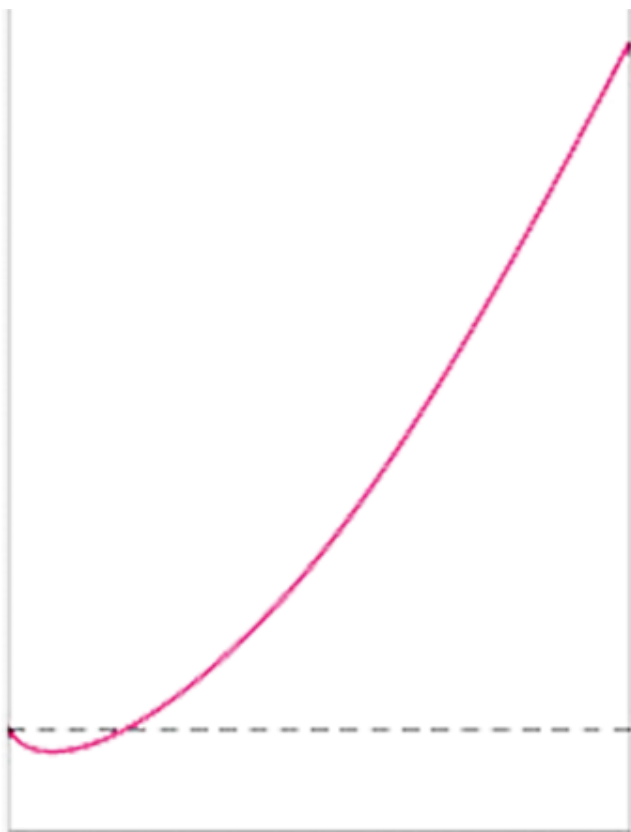


ΔG for 100% Reac \rightarrow 100% Prod is **positive** but 100% Reac \rightarrow mixture is **negative** so forward reaction can take place.

ΔG for 100% Prod \rightarrow 100% Reac **and** 100% Prod \rightarrow mixture is **more negative** so backward reaction is **favoured**

Equilibrium lies **over to the left** but **only slightly** since value of ΔG is **positive** but relatively **small**

Equilibrium position

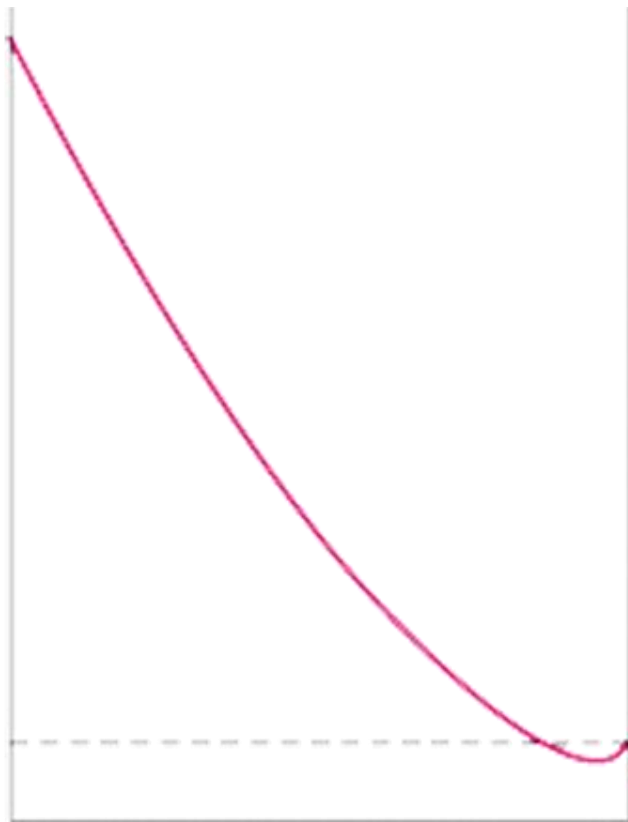


ΔG for 100% Reac \rightarrow 100% Prod is **very positive** but 100% Reac \rightarrow mixture is still **slightly negative** so forward reaction can take place.

ΔG for 100% Prod \rightarrow 100% Reac **and** 100% Prod \rightarrow mixture is **more negative** so backward reaction is **favoured**

Equilibrium lies **well over to the left** since value of ΔG is **positive** and relatively **large**

Equilibrium position



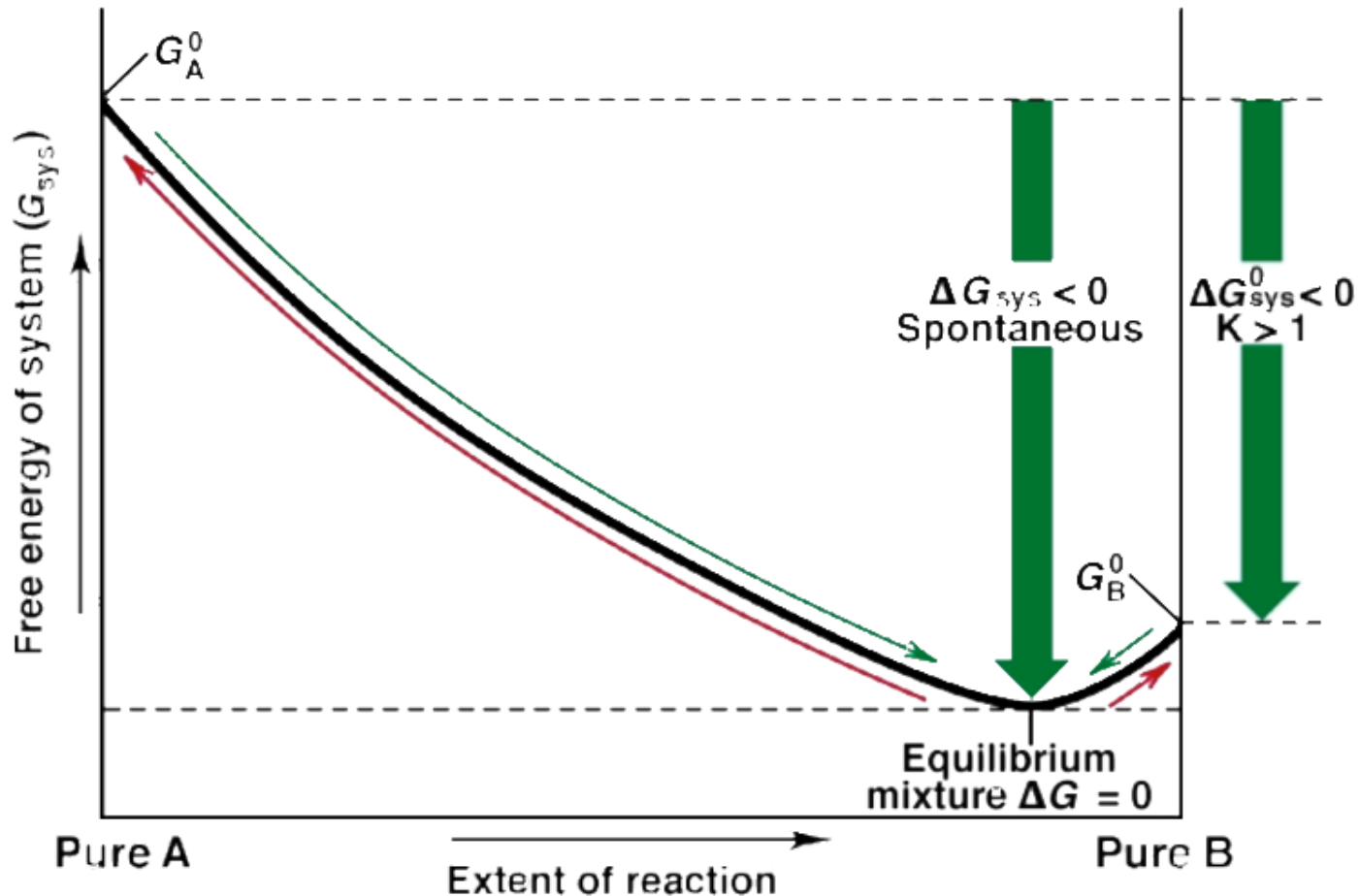
ΔG for 100% Reac \rightarrow 100% Prod is **very negative** but 100% Prod \rightarrow mixture is still **slightly negative** so backward reaction can take place.

ΔG for 100% Reac \rightarrow 100% Prod **and** 100% Reac \rightarrow mixture is **more negative** so forward reaction is **favoured**

Equilibrium lies **well over to the right** since value of ΔG is **negative** and relatively **large**

Equilibrium position

Free Energy and the Extent of Reaction



Equilibrium Position

There is a mathematical relationship:

$$\Delta G^\circ \equiv -RT \ln K$$

More simply:

Relationship Between the Standard Free-Energy Change and the Equilibrium Constant for a Reaction: $\Delta G^\circ = -RT \ln K$

ΔG°	$\ln K$	K	Comment
$\Delta G^\circ < 0$	$\ln K > 0$	$K > 1$	The equilibrium mixture is mainly products.
$\Delta G^\circ > 0$	$\ln K < 0$	$K < 1$	The equilibrium mixture is mainly reactants.
$\Delta G^\circ = 0$	$\ln K = 0$	$K = 1$	The equilibrium mixture contains comparable amounts of reactants and products ($K = 1$ for 1 M concentrations and 1 atm partial pressures).

Thermodynamic Limits



Thermodynamics can predict whether a reaction is **feasible** or not.

Thermodynamics can predict the **conditions** necessary for a reaction to be feasible.

Thermodynamics can predict the **position of equilibrium**

Thermodynamics **cannot** predict **how fast** a reaction might be.

